10/009855 JC09 Rec'd PCT/PTO 25 OCT 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF EXPRESS MAILING Attorney Docket No.: UDL1P067 I hereby certify that this paper and the documents and/or fees referred to as attached therein are being deposited with the United States Postal Service on First Named Inventor: October 25, 2001 in an envelope as "Express Mail Post Office to Addressee" service under 37 CFR §1.10, Mailing Label Number EL580853794US, addressed to the Commissioner for Patents, Washington, Thomas Hainsworth urelia Sanchez TRANSMITTAL LETTER FOR A PCT INTERNATIONAL APPLICATION ENTERING THE NATIONAL STAGE IN THE U.S. AS A DESIGNATED or ELECTED OFFICE UNDER 35 USC 371 Commissioner for Patents Box PCT Attention: DO/EO Washington, DC 20231 Transmitted herewith are the papers required to enter the national stage in the U.S. as a designated office/elected office for the following PCT international patent application: INTERNATIONAL APPLICATION NUMBER: PCT/GB00/01449 Int'l Filing Date: April 27, 2000

Thomas Hainsworth and Derek Walker

A Designated Office (No Demand was filed - See 37 CFR 1.494)

An English Translation of the International Application

A translation of amendments made under PCT Article 19

A Combined Declaration and Power of Attorney
A copy of amendments made under PCT Article 19

An Elected Office (A Demand for Preliminary Examination was Filed - See 37 CFR 1.495)

A copy of the international application (if this line is not checked, the international application was previously communicated by the International Bureau or the international application was

st Priority Date:

Inventor(s):

Enclosures:

For:

April 28, 1999

FIRE RESISTANT TEXTILE MATERIAL

originally filed in the USPTO).

preliminary examination report)
Information Disclosure Statement

The United States Patent Office is: (select one)

A translation of amendments made under PCT Article 34 (annexes to the international

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An Assignment of the Invention to:	
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A Preliminary Amendment	
A copy of the International Search Report	
A copy of the Preliminary Examination Report	
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Applicant is entitled to Small Entity Status under 37 C.F.R. §1.27. BASIC FEE	40.00
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The Commissioner is authorized to charge any fees beyond the amount required, or to credit any overpayment, to Deposit Account No. 500388 (Commission)	nt enclosed which may be Order No. UDL1P067).
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FIRE RESISTANT TEXTILE MATERIAL

This invention relates to fire resistant textile materials and garments made from these materials. The invention relates particularly but not exclusively to articles of clothing for use by fire fighters and for textiles for manufacture of such clothing.

European legislation requires employers to provide garments which protect their employees against hazards to which they may be exposed. Clothing for protection against heat and flame must pass minimum performance requirements for flame, radiant heat, heat resistance, tensile and tear strength, abrasion resistance and penetration by water and liquid chemicals. The assembled garments must achieve levels of resistance to heat transfer by both flame and radiant heat.

One of the most effective ways to reduce second and third degree burns is to make sure that the barrier of protective clothing between the heat source and the skin remains intact during exposure. This is referred to as the break open resistance or non-break open protection.

An object of the present invention is to optimise thermal protection offered by the fabric. We have discovered that this can be achieved through use of enhanced fabrics design and fibre utilisation.

Outer textile materials for fire fighting clothing have previously been manufactured from 100% meta-aramid or polyamideimide, blends of meta-aramid and para-aramid fibres or by use of core spun yarns or staple mixtures with polyparaphenylene terephthalamide copolymer or fibres comprising para-aramid cores with meta-aramid or polyamideimide covers. The combination of these fibres in the fabric enhances the non-break open protection of the product. However meta-aramid and polyamideimide fibres shrink, consolidate and thicken when exposed to a high temperature heat source. The presence of para-aramid or polyphenylene terephthalamide copolymer in either the fibre blend or as a core can be used to prevent fibre shrinkage and consequent breaking open of the garment. However the inclusion of para-aramid fibre in the blend has been found to be insufficient in tightly woven fabrics to prevent breaking open. Consequently there is a need for improved textile materials for manufacture of fire fighting garments and the like.

AT 34 ALBERT

Fire fighting garments have been made from a plurality of textile layers, including an outer layer of woven meta-aramid fibre, for example as manufactured under the trade mark Nomex. Break open protection may be afforded by blending with para-aramid fibres, eg as manufactured under the trade mark Kevlar and as disclosed in US 3063966 and US 3506990. However charring of such blends may lead to cracking and embrittlement with consequent deterioration of physical properties.

DE-A-29611356 discloses a protective glove, resistant to cutting wherein a two layer weave has an outer side of meta-aramid fibres and an inner side of para-aramid fibres.

According to the present invention a fire resistant textile material comprises a woven face fabric composed of fibres selected from meta-aramid, polyamideimide and mixtures thereof, the fabric including a woven mesh of low thermal shrinkage fibres.

Use of low thermal shrinkage fibres in accordance with the present invention increases the residual tensile strength of the textile material following exposure to flame or a radiant heat source. Low thermal shrinkage fibres in accordance with this invention may be defined as a fibre which exhibits not more than 6% shrinkage when exposed to a temperature of 400°C for a period of 5 seconds.

Low thermal shrinkage fibres in accordance with the present invention may be selected from the following materials:

polyparaphenylene terephthalamide (para-aramid eg Kevlar), polyparaphenylene terephthalamide copolymer, polyamide imide, copolyimide, phenolic fibres obtained by cross-linkage of phenolaldehyde resin and containing more than 70% carbon, polybenzimidazole, polyetheretherketone, high tenacity viscose, silicon carbide both with a core and with an organic precursor, ceramic fibres including alumina, alumina silicate and borosilico aluminate; and glass fibres including E glass, C glass, D glass and R glass. Mixtures of the aforementioned fibres may be employed.

Preferred low shrinkage fibres are selected from para-aramid, polyparaphenylene terphthalamide copolymers; polyamide imide; carbon fibres and mixtures thereof.

Fibres or yarns composed of 100% polyparaphenylene isophthalamide metaaramid (eg Nomex) shrink upon exposure to high temperatures, for example in excess of 100 Apr 101 Ap

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295EC. This shrinkage can result in a whole garment exposed to a flame. The low thermal shrinkage fibres, for example para-aramid fibres or yarns do not shrink to the same extent on exposure to this temperature. (The thermal shrinkage of Kevlar is about 3%,

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whilst the thermal shrinkage of Nomex is about 24%). If the two fibres or yarns are combined in a fabric, the shrinkage of the fabric may be controlled and/or restricted in such a way that the formation of holes, or break opening, is minimised. The direction of the distortion of the fabric when in the cross-sectional direction when exposed to a high temperature may be controlled so that the fabric becomes thicker. This control is achieved by use of a woven or warp knitted face fabric. This serves to increase the thermal protection afforded by the fabric and increases the number of seconds needed to raise the temperature on the inner side to a level which would create pain or a second degree burn on human skin or on the type of sensor used in Thermal Protection Procedure (TPP) testing.

Fire resistant fabrics in accordance with this invention confer a further advantage in comparison to fabrics composed of an intimate blend of meta-aramid and para-aramid fibres. Fabric formed from an intimate blend exhibits poor retention of the new appearance. The presence of low thermal shrinkage fibres on the surface of a garment, for example Kevlar results in formation of fine fibrils due to abrasion in use. Coloured fabrics, for example dark blue as used for fire fighters? tunics may develop light specks on the surface of the fabric. This gives an uneven appearance on a dark coloured garment. Fabric frosting is the term used to describe this effect.

The low shrinkage fibres are preferably disposed behind the face fabric. This minimises exposure of the strengthening fibres to the heat source.

Fabrics in accordance with the present invention also have the advantage that degradation of the low thermal shrinkage fibres, which are more susceptible to ultra-violet light degradation than other fibres, is reduced because they are not located on the outer surface of the fabric.

In preferred embodiments of the invention the low thermal shrinkage fibres form an interwoven backing scrim on the back of the face fabric. The low thermal shrinkage fibres preferably comprise para-aramid or polyparaphenylene terephthalamide copolymer, eg Kevlar yarns. The thickness of the yarn may be selected in accordance with the resultant mass and weave of the finished fabric. The resultant mass (g/m²) will vary dependent on the particular end use but will generally be within the range 150 to 300 g/m².

The woven fabric is preferably a combination of a face fabric into which is interwoven a backing scrim. The weave of the face fabric may vary dependent upon the mass and end use required. The interweaving of the backing scrim will be dependent on the weave of the face fabric and the thermal performance required.

Fabrics in accordance with this invention may be produced by interweaving yarns which have been spun and plied or core spun from staple fibres and/or multifilament fibres which may comprise 100% meta-aramid, 100% para-aramid, 100% polyamide imide or intimate blends of any combination of these fibres.

The interweaving of the selected yarns may be such that a closely woven fabric suitable for use as the outer face of a garment is combined with a loosely woven fabric which is suitable for use as the reverse side of the garment.

The selection of fibres and yarns which may be incorporated into fabrics in accordance with this invention will take account of the different shrinkage properties of these fibres and the particular requirements of the final fabric. A combination of high and low shrinkage fibres may be chosen. For example meta-aramid face fabric with a thermal shrinkage of approximately 24% and a para-aramid backing scrim or mesh with a thermal shrinkage of approximately 3% may be employed.

The proportion and count of face side yarns to reverse side yarns may be determined by the required weight of the final fabric, the interlacing of the face weave and the degree of effectiveness required from the properties of the reverse side yarn.

In a preferred embodiment the face yarns count may be in the range of resultant 15 to 50 Nm (Numero metric, including single or multiple folding of yarns), preferably 20 to 41 Nm. The reverse side yarns count may be in the range 25 to 150 Nm, preferably 40 to 60 Nm (Numero metric, including single or multiple folding of yarns).

Independently the proportion or ratio of face to back yarns by number may be 1 to 20:1, preferably 6 to 12:1.

The interlacing of the face weave may be determined by the desired appearance and the physical properties required of the final fabric. This interlacing may be any of a number of designs known to those skilled in the art. The preferred face weaves are plain weave, plain weave rip stop, twill weave rip stop or straight twill weaves and their

derivatives. Figure 1 shows weaving plans for five preferred fabrics. Plan 1 is a plain weave face; plan 2 is a plain weave rip stop face; plan 3 is a 2 x 2 twill face; and plan 4 is a 2 x 1 twill rip stop face. With these constructions the proportions of warp and weft yarns may be more evenly distributed to afford a more balanced structure. Other weaves may be used if the requirements to do so arises. The degree of interlacing between the face side yarns and the reverse side yarns is important to achieve a fabric which maximises the different properties of these yarns, gives a level surface and pleasing appearance and yet can be woven with the highest possible efficiency.

In a preferred method the yarns for the warps of both the face and reverse sides of the fabric may be assembled in the specified proportions and order of working by the sectional warping process onto one or two warped beams jointly having the total number of ends required to weave the final fabric.

The west yarns may be inserted across and interlaced with the warp yarns in the specified proportions, order of working and density selected to produce the required face and reverse side weaves.

Differential tension may be applied to the face and reverse side yarns during the weaving process and during the insertion of the weft. This is important to compensate for the varying degrees of elongation which are inherent in the different types of fibres used in those yarns and which are important to the properties of the fabric of this invention.

A preferred weaving machine which may be used to produce fabric of this invention is one that will supply the face and back warp yarns from individual warp beams at different fed rates to compensate for the varying degrees of elongation and the varying inter-lacings of the face fabric yarns and reverse side yarns.

A preferred weaving machine should also have electronic filling control braking for independent weft tensioning to compensate for the varying degrees of elongation and the varying inter-lacings of the face fabric yarns and reverse side yarns. The differential tensioning set to weave fabric of this invention may require a breaking force of 35% for the face yarn and 75% for the reverse side yarn.

Warp knitted fabrics may also be provided in accordance with this invention. Previously known fire fighting garments comprise a composite of three textile layers, an outer fabric, a moisture barrier and a quilted thermal lining. The present invention may reduce the need for use of three layers, or allow the total weight of those three layers to be reduced.

The invention is further described by means of example but not in any limitative sense

Example 1

A textile material in accordance with the present invention (referred to as specification EX276) was woven using a self-stitched double construction, with a blend of 93% meta-aramid, 5% para-armaid and 2% antistatic fibre (Nomex Delta C) 2 by 1 twill face and a 100% para-aramid (Kevlar) plain weave back. It is woven in the proportion of six face threads to one back thread.

Test Method

The fire resistance of textile materials in accordance with the present invention was determined using the following test method.

The Thermal Protective Performances of fabrics in accordance with this invention were measured by the Thermal Protective Performance (TPP) test. This test is a laboratory test to assess how well a fabric or combinations of fabric provides a barrier to and insulation from heat/flame.

In a "typical" flash fire the heat flux may be in the region of 80 kW/m². The test method used a heat source with a heat flux of 80 kW/m² (2 cal/cm²/sec) made up of approximately 50% radiant and 50% convective heat exposed to the underside of the sample. Sensors are employed to measure a rise in temperature on the other side of the sample. This rise in temperature is correlated, via earlier research work, to the tolerance of human skin and susceptibility to pain and second degree burns as used in TPP testing where "Stoll Curves" are used for the correlation.

The TPP test was used to measure heat energy required on outer surface (underside) of fabric or fabric combination to cause second degree burns at the back of the fabric or fabric combination. The number of seconds required with a fixed level of energy

(2 cal cm²sec⁻¹) to reach pain and second degree burns is also determined.

TABLE 1

Description of Fabric Assembly	Pain (/sec)	2 nd degree	TPP	Fabric &
		burn (sec)	(Wcm ⁻²)	Fibre Factor
EX276 (219 g/m ²)				
PTFE membrane laminated to				
aramid felt (Goretex E89)				
aramid felt (Nomex Felt)				
aramid liner (Nomex III)				
Total weight: 620 g/m ²	14.5	20.9	41.9	6.8
Quality 1166 Nomex Delta C (219 g/m²)				
Goretex E89				
Nomex Felt				
Nomex III				
Total weight: 620 g/m ²	13.0	18.3	36.5	5.8
Quality 1186 PBI Gold (224 g/m²)				
Goretex E89				
Nomex Felt				
Nomex III				
Total weight: 625 g/m ²	13.2	19.5	39.1	6.3
Quality 1191 Nomex Delta T (219 g/m²)				
Goretex E89				
Nomex Felt				

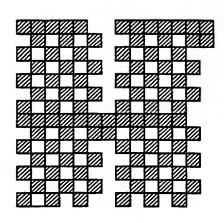
Nomex III				
Total weight: 620 g/m ²	13.5	19.5	39	6.3

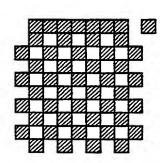
The results are shown in Table 1. These indicated that the energy required to give second degree burns at the back of the fabric was approximately 14.8% higher for the textile material in accordance with the present invention referred to as quality EX276 than a fabric of equivalent weight (Quality 1166) manufactured solely from the same intimate blend of fibres as the face fabric of EX276.

CLAIMS

- 1. A fire resistant textile material comprising a woven faced or warp knitted fabric composed of fibres selected from meta-aramid, polyamideimide and mixtures thereof, the fabric including a woven mesh back of low thermal shrinkage fibres, wherein the low thermal shrinkage fibres form an interwoven backing scrim on the face fabric, and wherein the ratio of face to back yarns by number is in the range 6:1 to 12:1.
- 2. A textile material as claimed in claim 1, wherein the low thermal shrinkage fibres are selected from fibres having a shrinkage of less than 6% at 400°C
- 3. A textile material as claimed in claim 2, wherein the low thermal shrinkage fibres are selected from polyparaphenylene terephthalamide (para-aramid eg Kevlar), polyparaphenylene terephthalamide copolymer, polyamide imide, copolyimide, phenolic fibres obtained by cross-linkage of phenolaldehyde resin and containing more than 70% carbon, polybenzimidazole, polyetheretherketone, high tenacity viscose, silicon carbide both with a core and with an organic precursor, ceramic fibres including alumina, alumina silicate and borosilico aluminate; and glass fibres including E glass, C glass, D glass and R glass and mixtures thereof.
- 4. A textile material as claimed in any preceding claim wherein the low thermal shrinkage fibres are disposed behind the face fabric.
- 5. A textile material as claimed in any preceding claim, wherein the low thermal shrinkage fibres comprise para-aramid yarns.
- 6. A textile material as claimed in any preceding claim, wherein the mass of the textile material is within the range 150 to 300 g/m².

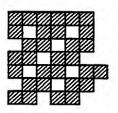
- 7. A textile material as claimed in any preceding claim, wherein the woven fabric is a combination of a face weave on which fabric is interwoven using a backing scrim.
- 8. A woven textile material as claimed in any preceding claim, wherein the face yarns count is in the range of resultant 15 to 50 Nm.
- 9. A woven textile material as claimed in claim 8, wherein the face yarns count is in the range of resultant 20 to 41 Nm.
- 10. A woven textile material as claimed in claim 8 or 9, wherein the reverse side yarns count is in the range 25 to 150 Nm.
- 11. A woven textile material as claimed in claim 10, wherein the reverse side yarns count is in the range 40 to 60 Nm.
- 12. A woven textile material as claimed in any preceding claim, wherein the face weave is selected from: plain weave, plain weave rip stops, straight twills, twill weave rip stops and their derivatives.

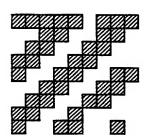




Plan no. 1

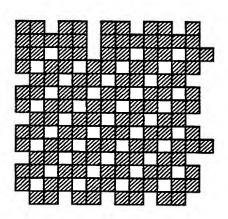






Plan no. 3

Plan no. 4



Plan no. 5

FIG. 1

DECLARATION AND POWER OF ATTORNEY FOR ORIGINAL U.S. PATENT APPLICATION

Attorney's Docket No. <u>UDL1P067</u>

As a below-named inven	tor, I hereby declare that:		
My residence, post office	e address and citizenship are	as stated below next to my name.	
plural names are listed be	iginal, first and sole inventorelow) of the subject matter value MATERIAL the speci	which is claimed and for which a pa	or an original, first and joint inventor (if atent is sought on the invention entitled:
(check one)	1. is attached hereto		
Tree grows g	 U.S. Application and was amended 3. was filed on April International PCT and was amended 	Application No. <u>PCT/GB00/01449</u> l on	 as
amended by any amendm	nent referred to above. To disclose information which		l specification, including the claims, as his application in accordance with Title
for patent or inventor's contain the United States, 1	ertificate, or § 365(a) of any listed below and have iden	y PCT International application which tified below, by checking the box,	or § 365(b) of any foreign application(s) ch designated at least one country other any foreign application for patent or of the application on which priority is
9909850.1 (Application No.)	Great Britain (Country)	April 28, 1999 (Filing Date)	Priority Benefits Claimed? Yes XNo
(Application No.)	(Country)	(Filing Date)	Yes No
Provisional Application	(s)		
I hereby claim the benefit	t under 35 U.S.C. §119(e) of	any United States provisional applic	ration(s) listed below:
(Application No.)	(Filing D	rate)	
(Application No.)	(Filing D	rate)	

Atty. Dkt. No.: UDL1P067

Page 1 of 2

(Revised 03/00)

Frior U.S. Application(s)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application No.)	(Filing Date)	(Status - patented, pending, abandoned)	
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Power of Attorney			
		المراجعة والمعاطية المحمولين والمرايين والمياني والراجعة	_
And I hereby appoint the	law firm of Beyer Weaver & Thomas, L	LP and all practitioners who are associated with the Custo	me
		ation and to transact all business in the Patent and Trader	narl
Office connected therew	itn.		
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